

PTO 93-3316

Japan, Kokai
63-195149

TRANSPARENT ELECTRICALLY CONDUCTIVE FILM
[Tomei Dendomaku]

Mamoru Mizuhashi, et al

63-195149

or

App # 02-27368

UNITED STATES PATENT AND TRADEMARK OFFICE
Washington, D.C. August 1993

Translated by: Diplomatic Language Services, Inc.

(19) JAPAN

(12) Official Gazette For Unexamined Patents

(11) Kokai No.: 63-195149

(43) Kokai publication date: August 12, 1988

(21) Application No.: 62-27368

(22) Application date: February 10, 1987

(51) IPC: C 03 C 17/23
H 01 L 31/04

(72) Inventors: Mamoru Mizuhashi, Masafumi Tada, and Kazuyuki Matsui

(71) Applicant: Asahi Glass KK

(54) TRANSPARENT ELECTRICALLY CONDUCTIVE FILM

1. Title of the invention

Transparent Electrically Conductive Film

2. Claims

(1) A transparent electrically conductive film with improved corrosion resistance characterized by formation of a protective film consisting of titanium carbide or hydrogen-doped titanium carbide, on the surface of a transparent electrically conductive film whose main component is indium oxide or tin oxide.

(2) A transparent electrically conductive film according to claim (1), characterized by formation of a protective film consisting of titanium carbide containing 50% or less of hydrogen in terms of atomic ratio.

(3) A transparent electrically conductive film according to claim (1) characterized by a protective film whose thickness is 10 to 100Å.

3. Detailed explanation of the invention

(Industrial application)

The present invention relates to a transparent electrically conductive film which possesses corrosion resistance, and in particular, to a transparent electrically conductive film which is optimal as a solar battery substrate.

(Prior art)

In general, transparent electrically conductive films which are transparent in the visible light spectrum and which possess electrical

*Numbers in the margin indicate pagination in the foreign text.

conductivity are used as transparent electrodes in new display systems such as liquid crystal displays and EL displays, and as transparent electrodes in amorphous silicon solar batteries. They are also used for purposes of static prevention in photo masks and other varied applications by conducting film formation on transparent glass substrates. As the material for such transparent electrically conductive film, indium oxide and tin oxide which are used. Indium oxide in particular, is capable of bringing about lower resistance, and by adding a tin oxide content, specimens of approximately $10^{-4}\Omega$ cm can presently be obtained.

(Problems to be solved by the invention)

Thus, transparent electrically conductive film, and particularly indium oxide film, possesses superior properties with regard to electrical conductivity, but when examined from the standpoints of corrosion resistance and reduction resistance, it is found to be extremely weak. For example, when a film of indium oxide with a /246 thickness of 500-1000Å and which has been deposited and formed on a glass sheet is soaked in hydrochloric acid of 100% concentration, it is dissolved in 1 to 3 seconds and becomes utterly unusable. Moreover, indium oxide is an oxygen deficient type of transparent electrically conductive film, and possesses donor type electrical conductivity. With regard to this film, since the bonding of indium and oxygen is weak, when ion bombardment is conducted in a high temperature atmosphere containing hydrogen or in plasma, the oxygen is liberated, and the metallic indium is precipitated and devitrified. This constitutes a

major problem when using indium oxide film as a solar battery semiconductor film, because, presently, the use of amorphous silicon film as solar battery semiconductor film is the industry mainstream, and this amorphous silicon film is manufactured by the plasma CVD method using hydrogen plasma. As a means for resolving the pertinent problem points, one can conceive of forming another layer as a blocking layer on top of the indium oxide layer.

It has been proposed to use a tin oxide film as this blocking layer (Japanese patent 58-218704), but it is inadequate from the standpoint of plasma reaction resistance.

(Mechanism for solving the problems)

The present invention was made in order to resolve the above-mentioned problem points, and offers a transparent electrically conductive film with improved corrosion resistance characterized by formation of a protective layer consisting of titanium carbide or hydrogen-doped titanium carbide on the surface of a transparent electrically conductive film whose main component is indium oxide or tin oxide.

Below, the present invention is explained in further detail.

Fig. 1 and Fig. 2 are drawings which show the mode of execution of the transparent electrically conductive film pertaining to the present invention. (1) is the substrate, (2) is the transparent electrically conductive film whose main component is indium oxide or tin oxide, (3) is the protective layer consisting of titanium carbide, or titanium carbide doped with hydrogen, and (4) shows the alkaline barrier film.

In the present invention, as the transparent electrically conductive film whose main component is indium oxide, one uses a tin-doped indium oxide electrically conductive film to which electrical conductivity has been imparted and in which tin is contained relative to indium oxide in a range of 0.5-30 weight %, and preferably 5-10 weight %. As the transparent electrically conductive film whose main component is tin oxide, a fluorine-doped tin oxide electrically conductive film to which electrical conductivity has been imparted and in which fluorine is contained relative to tin oxide in a range of 0.1-5 weight % can be used, and preferably 0.3-2 weight %, or one uses an antimony-doped tin oxide electrically conductive film to which electrical conductivity has been imparted and in which antimony is contained relative to tin oxide in a range of 0.1-30 weight %, and preferably 0.3-5 weight %.

The pertinent tin-doped indium oxide electrically conductive film can be manufactured by the sputtering method or the vacuum deposition method; the fluorine-doped tin oxide electrically conductive film can be manufactured by the CVD (chemical vapor deposition) method, the sputtering method, the vacuum deposition method, or the solution spray method; and the antimony-doped tin oxide electrically conductive film can be manufactured by the CVD method, the sputtering method, the vacuum deposition method, or the solution spray method. The film thickness of the pertinent transparent electrically conductive film is determined by the resistance value and the optical properties one is seeking to obtain, but will ordinarily be in a range from 500Å to 2μm.

As the substrate (1) on which the said transparent electrically conductive film (2) is formed, from the standpoints of transparency,

optical properties, durability and electrical properties, it is preferable to use alkaline glass plates such as soda-lime silicate glass plate, aluminosilicate glass plate, borosilicate chloride glass plate, lithium aluminosilicate glass plate, etc., low alkaline content glass plates or non-alkaline glass plates, and quartz glass plates. In certain cases, one can also use transparent plastic plates or transparent plastic films. With regard to alkaline glass plates such as soda-lime silicate glass plate, or low alkaline-content glass plates, since it sometimes happens that the alkaline component of the surface dissolves and generates haze (blurring) in the transparent electrically conductive film formed on top of it, for purposes of preventing this, it is preferable to form an alkaline barrier film (4) whose main components are oxides such as SiO_2 , Al_2O_3 , ZrO_2 , etc. on the surface of the said glass plate on which the transparent electrically conductive film is formed.

In the present invention, a protective film consisting of titanium carbide is formed in order to improve the corrosion resistance, and particularly the plasma resistance, of the transparent electrically conductive film whose main component is indium oxide or tin oxide. It is particularly preferable to use a protective film consisting of titanium carbide which has been doped with hydrogen. As the pertinent hydrogen-doped titanium carbide film, a film consisting of titanium carbide which contains hydrogen in an atomic ratio of 50% or less is optimal, and it is particularly preferable to use a titanium carbide film which contains hydrogen in an atomic ratio of 1 to 30% so as to adequately demonstrate the effects of hydrogen content. /247

Titanium carbide is a compound which possesses a unit lattice of the same shape as common salt; the titanium atoms occupy the position of the chlorine ions and the carbon atoms occupy the position of the sodium ions. It possesses the average electrical conductivity of metal, and metallic luster; it is opaque, and possesses the properties of an alloy.

The delocalization of outer-shell electrons, which is a property of the metallic state, is not lost as a result of the penetration of carbon atoms into the titanium lattice. Moreover, it is clear from the rise in the melting point and in hardness that the titanium lattice has become more stable as a result of the penetration of the carbon. The hardness of the titanium carbide is Moh's hardness and is 8 to 10; this is close to that of the diamond, which is well-known for its chemical stability.

This property of chemical stability would seem to derive from the fact that a large amount of mechanical energy is required to bring about the reaction and dissociation of the carbon in the titanium lattice.

With regard to the resistance relative to plasma, since it is a non-oxide, change relative to reductive plasma would appear to be difficult. This means that, when forming the film of amorphous silicon for a solar battery, superior properties are exhibited in the case where titanium carbide is used as an overcoat on top of the transparent electrically conductive film.

As mentioned above, titanium carbide possesses delocalized outer-shell electrons which act as conduction electrons, and which show low resistance of 10^{-4} to $10^{-5}\Omega$ cm in terms of the bulk value. Consequently, even if the titanium carbide is applied as an overcoat onto the transparent electrically conductive film, it causes no difficulties at

all with regard to the sheet resistivity value of the solar battery substrate. Compared to the case where an oxide having no electrical conductivity whatsoever is applied as the overcoat, this fact is extremely advantageous. That is, the overcoat of titanium carbide exhibits superior properties from the standpoint of both plasma reaction resistance and the resistance value. Titanium carbide, however, possesses absorption in the visible light spectrum. With regard to film thickness, if one were to consider only the matter of improving the plasma reaction resistance of the transparent electrically conductive film which constitutes the base material, it would be acceptable to have to whatever extent possible, the film thickness of a film possessing properties close to bulk, and it would therefore not be necessary to make the film very thick. However, since the titanium carbide film is absorptive, if one does not make the film extremely thin, it is difficult to obtain the 75% or more of visible light transmittance of the entire overcoated transparent electrically conductive film, which is required for a solar battery substrate.

Yet, as film thickness becomes thinner, irregularities in its distribution tend to arise, and a deterioration in the property of plasma reaction resistance occurs. Accordingly, it is appropriate that the thickness of the protective film in the present invention be 10 to 100Å, and preferably 20 to 50Å.

Thus, as mentioned above, titanium carbide film has the advantage of not causing any rise in plasma resistance and the resistance value, but the disadvantage that a visible light transmittance of 70% or more is unobtainable due to its absorbency. Based on these points, it has

been found that in order to simultaneously satisfy high visible light transmittance, electrical conductivity and plasma resistance properties, it is effective to dope the titanium carbide with hydrogen, thereby causing the titanium carbide film to contain hydrogen. This produces a film in which visible light transmittance is improved without altering electrical conductivity and plasma reaction resistance. In particular, it is possible to simultaneously improve electrical conductivity, high transmittance and plasma reaction resistance by having the pertinent hydrogen contained in the titanium carbide film in an atomic ratio of 50% or less relative to the titanium carbide, and preferably in a range of 1 to 30%. If the hydrogen is contained in the titanium carbide film in an atomic ratio greater than 50%, insulation is increased, and in the case where it is formed as a protective film on top of the transparent electrically conductive film, its sheet resistivity as a solar battery is raised, impairing its performance. With regard to the protective film in the case where hydrogen is introduced into the titanium carbide, in order to adequately demonstrate its properties of improved visible light resistance and unaltered electrical conductivity and plasma reaction resistance, the introduction of the hydrogen in an atomic ratio of 1 to 30% is optimal. /248

Furthermore, in the case where the pertinent hydrogen is introduced into a titanium carbide film, a film thickness of 10 to 50Å is optimal.

As the method of forming the protective film consisting of titanium carbide or hydrogen-doped titanium carbide of the present invention, there is no need to limit oneself to specific techniques such as the vacuum deposition method or the sputtering method. Yet, in order to

produce an effective plasma reaction resistance with the above-mentioned film thickness, it is necessary to manufacture a film which is as close as possible to the properties of bulk, and for this purpose, it is desirable to use a plasma assist film manufacturing method such as the sputtering method, the ion plating method, or the plasma CVD method. Moreover, a finely made film which is close to bulk also seems to serve as an effective diffusion barrier. Furthermore, if the transparent electrically conductive film of the substrate is manufactured by the CVD method and if the protective film of the present invention is manufactured by the plasma CVD method, the on-line production of amorphous silicon becomes possible.

For example, in the case of film formation by the sputtering method, a titanium target or titanium carbide target is set up inside the vacuum chamber of the sputtering device, argon gas or argon gas and methane gas are introduced into this vacuum chamber, RF voltage is applied to the said target in this atmosphere, and sputtering is conducted to form the protective film consisting of titanium carbide on top of the transparent electrically conductive film. In order to form a protective film consisting of titanium carbide containing hydrogen, a titanium target or titanium carbide target is set up inside the vacuum chamber, argon gas, methane gas and hydrogen gas are introduced into this vacuum chamber, RF voltage is applied to the pertinent target in the above manner, and sputtering is conducted to form the film. In the case where sputtering is conducted with use of a titanium target in an atmosphere containing argon gas, methane gas and hydrogen gas, it is optimal to conduct the process in an atmosphere of 10 to 50 vol% methane

gas and 5 to 20 vol% hydrogen gas, with the remainder being argon gas. In the case where a titanium carbide target is used, it is optimal to have 5 to 60 vol% methane gas, 0 to 20 vol% hydrogen gas, with the remainder of argon gas.

Since the transparent electrically conductive film of the present invention has high plasma reaction resistance, all types of films can be formed on top of the pertinent transparent electrically conductive film by the plasma CVD method. Consequently, the said transparent electrically conductive film is optimal as a transparent electrode for use in an amorphous solar battery.

To manufacture the amorphous solar battery, one conducts sequential formation by the plasma CVD method of p-type amorphous Si film, i-type amorphous Si film, and n-type amorphous Si film on top of the transparent electrically conductive film of the present invention which is formed on top of, for example, a glass substrate.

(Embodiments)

Below, embodiments of the present invention are explained.

Embodiment 1

A metallic indium target containing 10at% (atomic ratio %) of tin and a titanium carbide sputtering target are each set up on a cathode inside the vacuum chamber of the sputtering device. A soda-lime silicate glass substrate with a thickness of 1.1mm whose surface has been cleaned by ceria polishing and water rinsing is inserted into the vacuum chamber, and the air is discharged by oil diffusion pump to 5.0×10^{-5} Torr or below. The substrate temperature is raised to 370°C.

Next, the vacuum chamber interior is filled with a mixed gas of $\text{Ar}:\text{O}_2 = 62:38$, the degree of vacuum is set to 2.2×10^{-3} Torr, DC voltage of 500V is applied to the tin-indium alloy target, and pre-sputtering is conducted for 10 minutes. After pre-sputtering, the shutter is opened and sputtering is conducted for 5 minutes to obtain a transparent In_2O_3 electrically conductive film containing 10at% of tin and possessing a film thickness of 4200Å. Next, without breaking the vacuum, the atmosphere inside the vacuum chamber is completely changed to a mixed gas of $\text{Ar}:\text{CH}_4 = 7:3$, and after adjusting the degree of vacuum to 2×10^{-4} Torr, DC voltage of 500V is applied to the titanium carbide target and sputtering is conducted for 2 minutes. The film thickness of the protective film of overcoated hydrogen-doped titanium carbide is approximately 60Å.

With regard to the transparent electrically conductive film obtained in this manner, the proportion of hydrogen doping is 15% in terms of the atomic ratio, and with a resistivity of $2.5 \times 10^{-4} \Omega \text{ cm}$ and a visible light transmittance of 80%, there is almost no change from /249 the non-overcoated state.

The ordinary plasma CVD device used in amorphous silicon manufacture is used here. After discharging the air from inside the chamber of the said device by an oil diffusion pump to a level of 1×10^{-5} Torr, SiH_4 gas and B_2H_6 gas diluted by hydrogen to 1000ppm are introduced into the chamber in a volume ratio of 1:10. After forming P-type amorphous silicon film on these transparent electrically conductive film substrates at a substrate temperature of 250°C and an RF output of 5W, the said amorphous silicon film undergoes etching with use of

hydrazine-hydrate, and the resistivity and transmittance of the transparent electrically conductive film are measured. The results show that, in contrast to a change of 1.6 times in resistivity and 0.9 times in transmittance with the non-overcoated film, there is no change at all in resistivity and transmittance with the film which has been overcoated by the protective film of hydrogen-doped titanium carbide of the present embodiment.

Embodiment 2

A metallic indium target containing 10at% (atomic ratio %) of tin and a pure metallic titanium sputtering target are each set up on a cathode inside the vacuum chamber of the sputtering device. A soda-lime silicate glass substrate (plate thickness: 1.1mm) with a silica alkaline barrier film whose surface has been cleaned by ceria polishing and water rinsing is inserted into the vacuum chamber, and the air is discharged by oil diffusion pump to 5.0×10^{-5} Torr or below. The substrate temperature is raised to 370°C. Next, the vacuum chamber interior is filled with a mixed gas of Ar:O₂ = 62:38, the degree of vacuum is set to 2.2×10^{-3} Torr, DC voltage of 500V is applied to the tin-indium alloy target, and pre-sputtering is conducted for 10 minutes. After pre-sputtering, the shutter is opened and sputtering is conducted for 5 minutes to obtain a transparent In₂O₃ electrically conductive film containing 10at% of tin and possessing a film thickness of 4200Å. Next, without breaking the vacuum, the atmosphere inside the vacuum chamber is completely changed to a mixed gas of Ar:CH₄ = 1:1, and after adjusting the degree of vacuum to 2×10^{-4} Torr, DC voltage of 500V is applied to the metallic titanium target. After conducting pre-sputtering for 1 minute,

sputtering is conducted for 2 minutes. The film thickness of the protective film of overcoated hydrogen-doped titanium carbide is approximately 80Å.

With regard to the transparent electrically conductive film obtained in this manner, the proportion of hydrogen doping is 10% in terms of the atomic ratio, and with a resistivity of $2.5 \times 10^{-4} \Omega \text{ cm}$ and a light transmittance of 80%, there is almost no change from the non-overcoated state.

The ordinary plasma CVD device used for amorphous silicon manufacture is used here. After discharging the air from inside the chamber of the said device by an oil diffusion pump to a level of $1 \times 10^{-5} \text{ Torr}$, SiH_4 gas and B_2H_6 gas diluted by hydrogen to 1000ppm are introduced into the chamber in a volume ratio of 1:10. After forming P-type amorphous silicon film on these transparent electrically conductive film substrates at a substrate temperature of 250°C and an RF output of 5W, the said amorphous silicon film undergoes etching with use of hydrazine-hydrate, and the resistivity and transmittance of the transparent electrically conductive film are measured. The results show that, in contrast to a change of 1.6 times in resistivity and 0.9 times in transmittance with the non-overcoated film, there is no change at all in resistivity and transmittance with the film which has been overcoated by the protective film of hydrogen-doped titanium carbide of the present embodiment.

Embodiment 3

First, a soda-lime silicate glass substrate (plate thickness 2.0mm) with silica alkaline barrier film, which possesses on its surface an

SiO₂ film (film thickness 800Å) formed by the CVD method as the alkaline barrier film, is adequately cleaned. This glass substrate is then inserted into the CVD device. After heating the glass substrate to 500°C, nitrogen gas containing tin tetrachloride of 1×10^{-2} l/minute as 1, 30 vapor (1.1×10^{-4} mol/minute) and water vapor, 1 methyl alcohol, and 1 hydrofluoric acid is sprayed onto this glass substrate surface to form a transparent electrically conductive film (film thickness 4000Å) consisting of tin oxide doped with 1.0wt% fluorine at approximately 5000Å/minute. Next, the glass substrate with the said transparent electrically conductive film is inserted into the vacuum chamber of the sputter device in which the titanium carbide sputtering target has been set, and after discharging the air until the vacuum chamber interior becomes 1.0×10^{-5} Torr, mixed gas of Ar:CH₄ = 7:3 is injected. After /250 adjusting the degree of vacuum to 5×10^{-4} Torr, RF voltage of 2.0KV is applied to the titanium carbide target. After 1 minute of pre-sputtering, sputtering is conducted for 1 minute. The film thickness of the overcoated hydrogen-doped titanium carbide is approximately 50Å. With regard to the transparent electrically conductive film obtained in this manner, the proportion of hydrogen doping is 10% in terms of the atomic ratio, and with a resistivity of 3.0×10^{-4} Ω cm and a transmittance of 80%, there is almost no change from the non-overcoated state.

The ordinary plasma CVD device used for amorphous silicon manufacture is used here. After discharging the air from inside the chamber of the said device by an oil diffusion pump to a level of 1×10^{-5} Torr, SiH₄ gas and B₂H₆ gas diluted by hydrogen to 1000ppm are introduced into the chamber in a volume ratio of 1:10. After forming P-

type amorphous silicon film on these transparent electrically conductive film substrates at a substrate temperature of 250°C and an RF output of 5W, the said amorphous silicon film undergoes etching with use of hydrazine-hydrate, and the resistivity and transmittance of the transparent electrically conductive film are measured. The results show that, in contrast to a change of 1.6 times in resistivity and 0.9 times in transmittance with the non-overcoated film, there is no change at all in resistivity and transmittance with the film which has been overcoated by the protective film of hydrogen-doped titanium carbide of the present embodiment.

Embodiment 4

A metallic indium target containing 10at% (atomic ratio %) of tin and a titanium carbide sputtering target are each set up on a cathode inside the vacuum chamber of the sputtering device. A soda-lime silicate glass substrate with a thickness of 1.1mm whose surface has been cleaned by ceria polishing and water rinsing is inserted into the vacuum chamber, and the air is discharged by oil diffusion pump to 5.0×10^{-5} Torr or below. The substrate temperature is raised to 370°C. Next, the vacuum chamber interior is filled with a mixed gas of Ar:O₂ = 62:38, the degree of vacuum is set to 2.2×10^{-3} Torr. DC voltage of 500V is applied to the tin-indium alloy target, and pre-sputtering is conducted for 10 minutes. After pre-sputtering, the shutter is opened and sputtering is conducted for 5 minutes to obtain a transparent In₂O₃ electrically conductive film containing 10at% of tin and possessing a film thickness of 4200Å. Next, without breaking the vacuum, the atmosphere inside the vacuum chamber is completely changed to Ar gas,

and after adjusting the degree of vacuum to 2×10^{-4} Torr, DC voltage of 500V is applied to the titanium carbide target, and sputtering is conducted for 2 minutes. The film thickness of the protective film of overcoated titanium carbide is approximately 80Å.

With regard to the transparent electrically conductive film consisting of titanium carbide which is obtained in this manner, with a resistivity of $2 \times 10^{-4} \Omega \text{ cm}$ and a visible light transmittance of 78%, there is almost no change from the non-overcoated state.

The ordinary plasma CVD device used in amorphous silicon manufacture is used here. After discharging the air from inside the chamber of the said device by an oil diffusion pump to a level of 1×10^{-5} Torr, SiH_4 gas and B_2H_6 gas diluted by hydrogen to 1000ppm are introduced into the chamber in a volume ratio of 1:10. After forming P-type amorphous silicon film on these transparent electrically conductive film substrates at a substrate temperature of 250°C and an RF output of 5W, the said amorphous silicon film undergoes etching with use of hydrazine-hydrate, and the resistivity and transmittance of the transparent electrically conductive film are measured. The results show that, in contrast to a change of 1.7 times in resistivity and 0.8 times in transmittance with the non-overcoated film, there is no change at all in resistivity and transmittance with the film which has been overcoated by the protective film of titanium carbide of the present embodiment.

(Effects of the invention)

As explained above, according to the present invention, it is possible to markedly improve the plasma reaction resistance in a

reducing atmosphere of transparent electrically conductive film, and particularly of indium oxide film and tin oxide film. This fact is extremely advantageous for purposes of using this film configuration as the substrate of a solar battery whose substrate is amorphous silicon.

Moreover, since the titanium carbide film or the hydrogen-doped titanium carbide film of the present invention is an extremely hard film, by using this film in the so-called irregular structural films of the solar battery, it can be made to work as a protective layer.

4. Brief explanation of the drawings

/251

Fig. 1 and Fig. 2 show cross-sectional drawings for purposes of explaining the transparent electrically conductive film pertaining to the present invention.

1: substrate, 2: transparent electrically conductive film, 3: protective film, 4: alkaline barrier film

Figure 1.

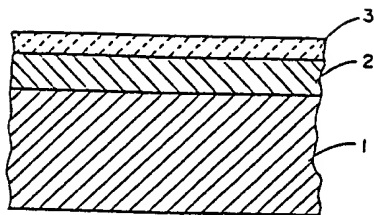


Figure 2.

